Electronic Supporting Information

Making a [Co_{24}] Metallamacrocycle from the Shuttlecock-like Tetranuclear Cobalt-calixarene Building Blocks

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Experimental Section

Materials and Measurements: *p-tert*-Butylthiacalix[4]arene (H_4TC4A) was synthesized by literature method[1] and other reagents were purchased from commercial sources and used as received. EDS analyses of Co, S and O and SEM examination were performed on a HITACHI S-4800 Scanning Electron Microscope. TGA measurement is carried out on a PYRIS DIAMOND. FTIR spectra (KBr pellets) were recorded on a Bruker Vertex 70 spectrometer. Powder X-ray diffraction (XRD) was determined by a Bruker D8 Advance diffractometer. Magnetic susceptibility measurements for **1** were performed on a Quantum Design MPMS XL-5 SQUID system in the temperature range of 2–300 K. Diamagnetic corrections for the sample and sample holder were applied to the data.

Synthesis of 1: Red single crystal blocks of **1** are obtained from reaction of the mixture of *p*-tert-butylthiacalix[4]arene (0.09g, 0.13 mmol), $Co(CH_3COO)_2 \cdot 4H_2O$ (0.1 g, 0.4 mmol), and 1, 2, 4-Triazole (0.014 g, 0.2 mmol), $CHCl_3$ (5 ml) and CH_3OH (5ml) in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at about 4 °C/h. The crystals were isolated by filtration and then washed with 1:1 methanol-chloroform. Yield: ca. 85 % with respect to H_4TC4A. The EDS analysis of **1** reveals that the molar ratio of Co and S is 5.40 : 5.43, comparable to the expected value (24 : 24 = 1 : 1) (Fig. S4). The elemental analysis for compound **1** deviated much from the calculated values due to easy lose of the involved solvent molecules in the lattices. The chloride anions in the structure would come from the decomposition of chloroform and its assignment was based on charge balance considerations and the long band distances (*ca.* 2.40 Å, larger than common Co-O distance).

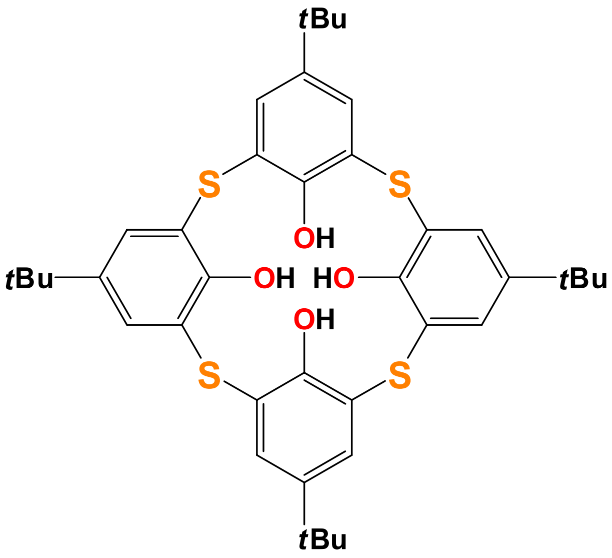
The acetate feed plays an important role in the formation of the title compound as indicated by further experiments:

Metal source	Amount of the metal source, mmol	Yield of **1** based on H_4TC4A, %	byproduct
$Co(CH_3COO)_2$	0.4	85	No
$Co(CH_3COO)_2$+$CoCl_2$	0.2 + 0.2	50	Co_4(TC4A)$_2$
$Co(CH_3COO)_2$ +NH_4Cl	0.4 + 0.1	90	Unidentified
$Co(CH_3COO)_2$ +NaCl	0.4 +0.1	90	Unidentified
$CoCl_2$	0.4	5	Co_4(TC4A)$_2$
$CoCl_2$+CH_3COONa	0.4 + 0.4	30	Co_4(TC4A)$_2$

The byproduct Co_4(TC4A)$_2$ (green needles) was determined by single-crystal X-ray diffraction which revealed that it is the analogous of Mn_4(TC4A)$_2$ reported by D. Luneau and co-workers.[2]

1 N. Iki, C. Kabuto, T. Fukushima, H. Kumagai, H. Takeya, S. Miyanari, T. Miyashi and S. Miyano, *Tetrahedron.*, 2000, **56**, 1437.

2. C. Desroches, G. Pilet, S. A. Borshch, S. Parola and D. Luneau, *Inorg. Chem.*, 2005, **44**, 9112.



Scheme S1 H_4TC4A

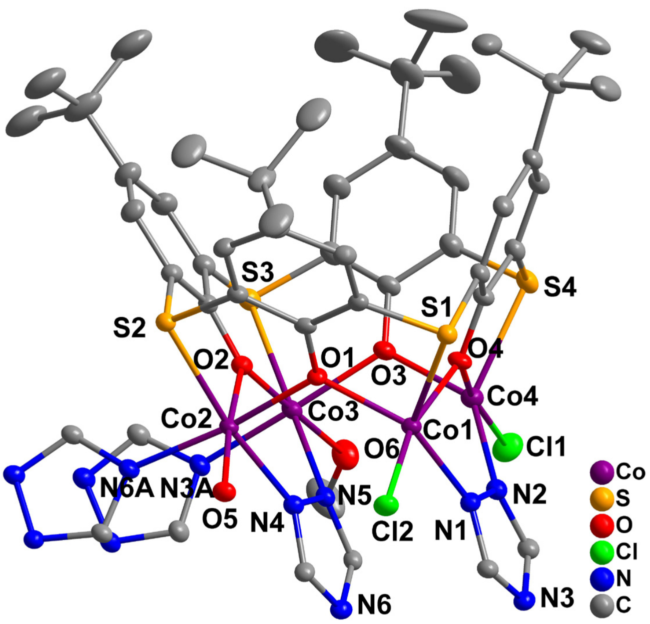


Figure S1 ORTEP diagram showing the coordination environment for cobalt atoms in **1**. A: -1/3+y,1/3-x+y,1/3-z.

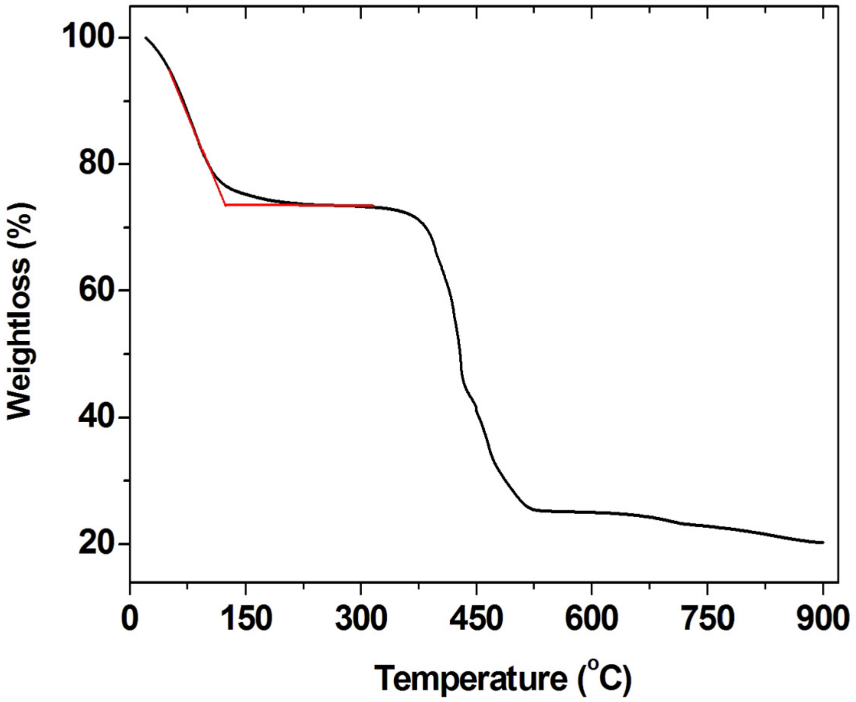


Figure S2. TG curve for compound **1.**

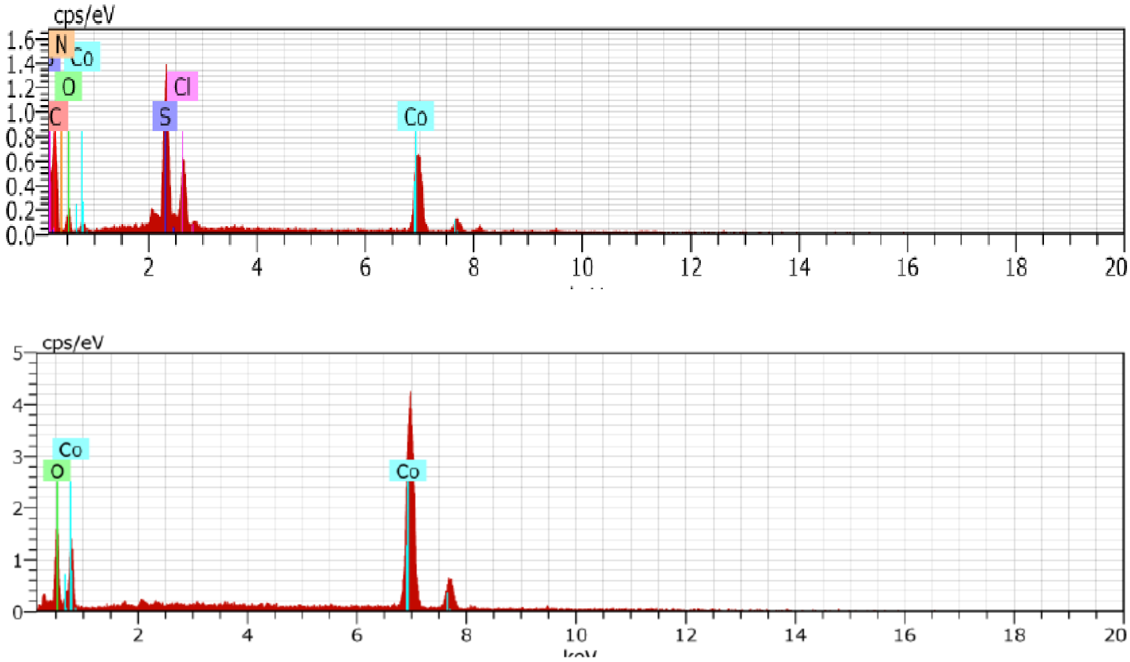


Figure S3. EDS plots of **1** (upper) and the CoO residual from the pyrolysis of **1** (bottom).

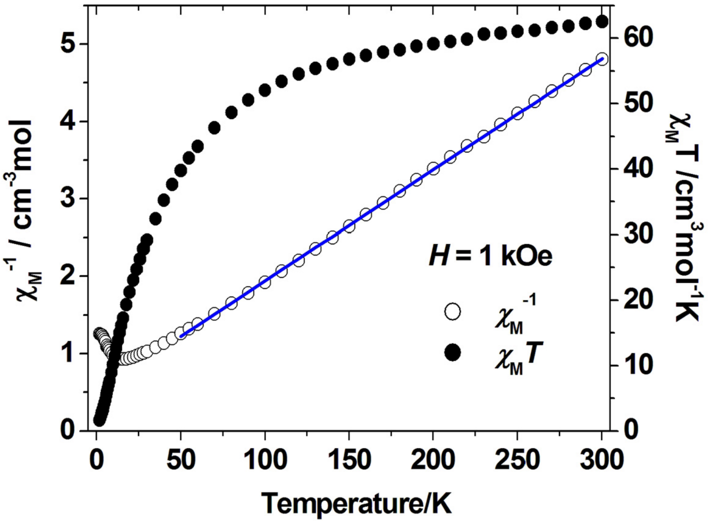


Fig. S4 Plots of $\chi_M T$ vs. T and $1/\chi_M$ vs. T for **1**. Blue solid line represents the Curie-Weiss fitting.

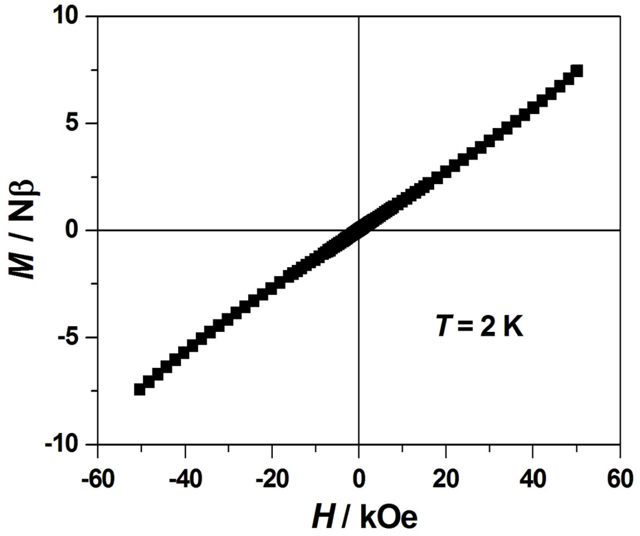


Fig. S5 Field-dependencies of magnetization of **1** at 2 K.

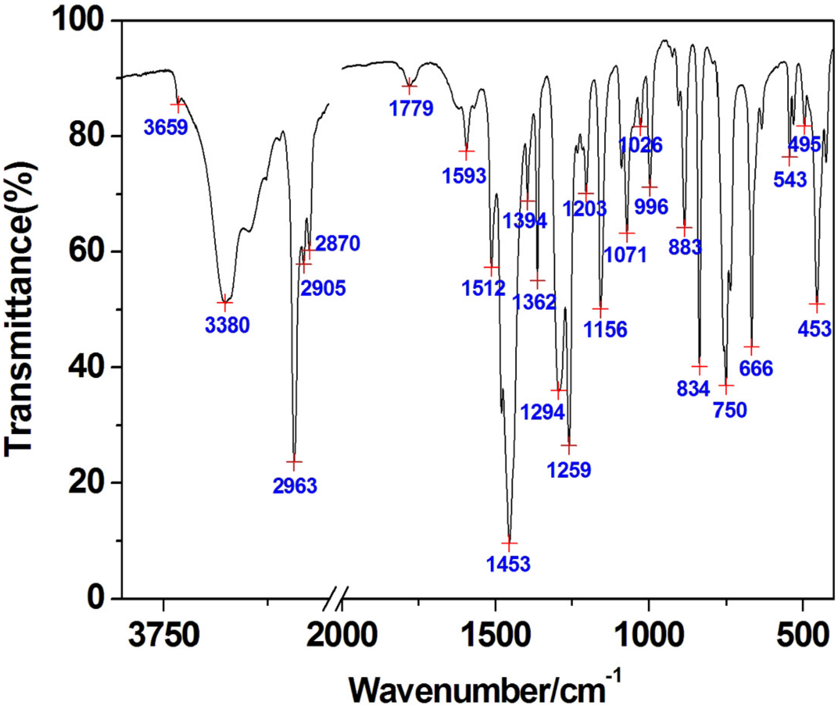


Figure S3. FT-IR spectra of compound **1**.

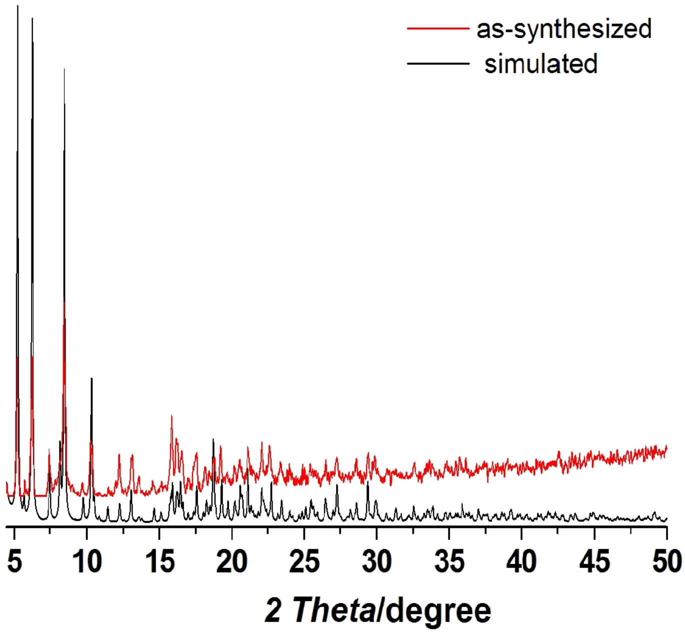


Figure. S5. Experimental XRD patterns of **1** exposed in air (red) and simulation patterns of **1** (black). Slight differences may arise from the loss of solvent molecules at room temperature.

Table S1. Selected distances (Å) and angles (°) for compound **1**

Co(1)–O(1)	2.000(3)	Co(4)–O(3)	2.001(4)
Co(1)–O(4)	2.025(5)	Co(4)–O(4)	2.032(4)
Co(1)–N(1)	2.051(4)	Co(4)–N(2)	2.040(5)
Co(1)–S(1)	2.4327(16)	Co(4)–S(4)	2.4378(19)
Co(1)–Cl(2)	2.369(2)	Co(4)–Cl(1)	2.368(2)
Co(2)–O(1)	2.097(3)	Co(3)–O(2)	2.042(4)
Co(2)–O(2)	2.026(5)	Co(3)–O(3)	2.070(4)
Co(2)–O(5)	2.127(5)	Co(3)–O(6)	2.153(5)
Co(2)–N(4)	2.081(4)	Co(3)–N(5)	2.117(5)
Co(2)–N(6)^d	2.121(6)	Co(3)–N(3)^d	2.096(6)
Co(2)–S(2)	2.4689(15)	Co(3)–S(3)	2.4781(19)
Co(1) ···Co(2)	3.5307(10)	Co(2) ···Co(3)	3.4857(12)
Co(3) ···Co(4)	3.5096(10)	Co(4) ···Co(1)	3.4618(12)
Co(1) ···Co(3)	4.6942(13)	Co(2) ···Co(4)	5.1799(9)
Co(1)–O(1)–Co(2)	119.02(16)	Co(2)–O(2)–Co(3)	117.92(18)
Co(3)–O(3)–Co(4)	119.1(2)	Co(4)–O(4)–Co(1)	117.09(19)